

TITLE OF THE INVENTION

COLOR-STABILIZED ELECTROCHROMIC DEVICES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation of co-pending U.S. Application Serial No.
5 10/208,525, filed July 30, 2002, which is a continuation-in-part of U.S. Application Serial
No. 10/035,721, filed October 25, 2001, now U.S. Patent No. 6,486,998 B2, which is a
continuation of U.S. Application Serial No. 09/652,983, filed August 31, 2000, now U.S.
Patent No. 6, 310,714 B1, which is a continuation of U.S. Application Serial No. 09/377,455,
filed August 19, 1999, now U.S. Patent No. 6,188,505 B1, which are hereby incorporated
10 herein by reference in their entirety.

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0002] The present invention relates in general to electrochromic devices, and more
particularly, to normally operating, color-stabilized electrochromic devices having an
15 electrochromic medium comprising one or more additives, which serve to substantially
preclude the formation of undesirable residual color within the electrochromic medium while
in its high transmission state.

2. Background Art

[0003] Electrochromic devices have been known in the art for several years. While
20 the utilization of electrochromic devices, such as electrochromic mirrors, has become
increasingly popular among, for example, the automotive industry, the development of
undesirable residual color within the electrochromic medium remains problematic.

[0004] Indeed, when a sufficient electrical potential difference is applied across the
electrodes of a conventional device, the electrochromic medium becomes intentionally

colored (i.e. a low transmission state) inasmuch as one or more of the anodic and the cathodic materials are oxidized and reduced, respectively. Specifically, the anodic materials are oxidized by donating electrons to the anode, and the cathodic materials are reduced by accepting electrons from the cathode.

5 [0005] For most commercially available devices, when the electrical potential difference is removed or substantially diminished, the anodic and cathodic materials return to their native or unactivated state, and in turn, return the electrochromic medium to its colorless or nearly colorless state (i.e. a high transmission state). The application and removal of an electrical potential difference is conventionally known as a single cycle of the electrochromic
10 device.

[0006] Scientists have observed that over a period of cycles and/or time, during normal operation of the electrochromic device, the electrochromic medium sometimes does not remain colorless in the high transmission state. In some instances, even in the absence of an electrical potential difference, either one or both of a portion of the anodic and cathodic
15 materials are oxidized or reduced respectively, thereby forming residual oxidized and/or reduced materials. The residual oxidized anodic materials and/or the residual reduced cathodic materials of the electrochromic medium can result in an undesired residual coloration of the electrochromic medium.

[0007] Factors that are believed to facilitate the formation of the undesired residual
20 oxidized anodic and/or reduced cathodic materials include, among other things, impurities within the medium, thermal and/or photochemical decomposition of one or more of the medium materials, and/or the permeation of water and/or oxygen into the electrochromic medium.

[0008] It is therefore an object of the present invention to provide an electrochromic

medium with a color-stabilizing additive that remedies the aforementioned detriments and/or complications associated with maintaining a colorless or nearly colorless electrochromic device while the device is in its high transmission state.

SUMMARY OF THE INVENTION

5 [0009] The present invention is directed to an electrochromic device, comprising: (a) a first substantially transparent substrate having an electrically conductive material associated therewith; (b) a second substrate having an electrically conductive material associated therewith; (c) an electrochromic medium contained within a chamber positioned between the first and second substrates which comprises: (1) a solvent; (2) a cathodic electroactive
10 material; (3) an anodic electroactive material, wherein at least one of the anodic and cathodic electroactive materials is electrochromic; and (4) a color-stabilizing additive, wherein the color-stabilizing additive is electroactive within a normal operating voltage of the electrochromic device; and (d) means associated with the color-stabilizing additive for maintaining an at least nearly colorless electrochromic device while the electrochromic device
15 is in an open circuit and/or zero potential state relative to the same device without the color-stabilizing additive.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] The invention will now be described with reference to the drawings wherein:

[0011] Fig. 1 of the drawings is a cross-sectional schematic representation of an
20 electrochromic device fabricated in accordance with the present invention;

[0012] Fig. 2 of the drawings is a two-dimensional plot showing the change in a^* as a function of exposure time to an oxidative environment for Experiments 1A-1B;

[0013] Fig. 3 of the drawings is a two-dimensional plot showing the change in b^* as a function of exposure time to an oxidative environment for Experiments 1A-1B;

[0014] Fig. 4 of the drawings is a two-dimensional plot showing the change in a^* as a function of exposure time to an oxidative environment for Experiments 2A-2D;

[0015] Fig. 5 of the drawings is a two-dimensional plot showing the change in b^* as a function of exposure time to elevated temperatures for Experiments 2A-2D;

5 [0016] Fig. 6 of the drawings is a two-dimensional plot showing the change in a^* as a function of exposure time to elevated temperatures for Experiments 3A-3B;

[0017] Fig. 7 of the drawings is a two-dimensional plot showing the change in b^* as a function of exposure time to elevated temperatures for Experiments 3A-3B;

[0018] Fig. 8 of the drawings is a two-dimensional plot showing the change in a^* as a
10 function of exposure time to elevated temperatures for Experiments 4A-4B; and

[0019] Fig. 9 of the drawings is a two-dimensional plot showing the change in b^* as a function of exposure time to elevated temperatures for Experiments 4A-4B.

DETAILED DESCRIPTION OF THE INVENTION

[0020] Referring now to the drawings and to Fig. 1 in particular, a cross-sectional schematic representation of electrochromic device 100 is shown, which generally comprises first substrate 112 having a front surface 112A and a rear surface 112B, second substrate 114 having a front surface 114A and a rear surface 114B, and chamber 116 for containing electrochromic medium 124. It will be understood that electrochromic device 100 may comprise, for illustrative purposes only, a mirror, a window, a display device, a contrast enhancement filter, and the like. It will be further understood that Fig. 1 is merely a schematic representation of electrochromic device 100. As such, some of the components have been distorted from their actual scale for pictorial clarity. Indeed, numerous other electrochromic device configurations are contemplated for use, including those disclosed in U.S. Patent No. 5,818,625 entitled "Electrochromic Rearview Mirror Incorporating A Third Surface Metal Reflector" and U.S. Application Serial No. 09/343,345 entitled "Electrode Design For Electrochromic Devices," both of which are hereby incorporated herein by reference in their entirety.

[0021] First substrate 112 may be fabricated from any one of a number of materials that are transparent or substantially transparent in the visible region of the electromagnetic spectrum, such as, for example, borosilicate glass, soda lime glass, float glass, natural and synthetic polymeric resins, plastics, and/or composites including Topas[®], which is commercially available from Ticona of Summit, New Jersey. First substrate 112 is preferably fabricated from a sheet of glass having a thickness ranging from approximately 0.5 millimeters (mm) to approximately 12.7mm. Of course, the thickness of the substrate will depend largely upon the particular application of the electrochromic device. While particular substrate materials have been disclosed, for illustrative purposes only, it will be understood

that numerous other substrate materials are likewise contemplated for use – so long as the materials are at least substantially transparent and exhibit appropriate physical properties, such as strength to be able to operate effectively in conditions of intended use. Indeed, electrochromic devices in accordance with the present invention can be, during normal operation, exposed to extreme temperatures as well as exposed to substantial UV radiation, emanating primarily from the sun.

[0022] Second substrate 114 can be fabricated from similar materials as that of first substrate 112. However, if the electrochromic device is a mirror, then the requisite of substantial transparency is not necessary. As such, second substrate 114 may, alternatively, comprise polymers, metals, glass, and ceramics – to name a few. Second substrate 114 is preferably fabricated from a sheet of glass having a thickness ranging from approximately 0.5mm to approximately 12.7mm. If first and second substrates 112 and 114, respectively, are fabricated from sheets of glass, then the glass can optionally be tempered prior to or subsequent to being coated with layers of electrically conductive material (118 and 120).

[0023] One or more layers of electrically conductive material 118 are associated with rear surface 112B of first substrate 112. These layers serve as an electrode for the electrochromic device. Electrically conductive material 118 is desirably a material that: (a) is substantially transparent in the visible region of the electromagnetic spectrum; (b) bonds reasonably well to first substrate 112; (c) maintains this bond when associated with a sealing member; (d) is generally resistant to corrosion from materials contained within the electrochromic device or the atmosphere; and (e) exhibits minimal diffusion or specular reflectance as well as sufficient electrical conductance. It is contemplated that electrically conductive material 118 may be fabricated from fluorine doped tin oxide (FTO), for example TEC glass, which is commercially available from Libbey Owens-Ford-Co., of Toledo, Ohio,

indium/tin oxide (ITO), doped zinc oxide or other materials known to those having ordinary skill in the art.

[0024] Electrically conductive material 120 is preferably associated with front surface 114A of second substrate 114, and is operatively bonded to electrically conductive material 118 by sealing member 122. As can be seen in Fig. 1, once bonded, sealing member 122 and the juxtaposed portions of electrically conductive materials 118 and 120 serve to define an inner peripheral geometry of chamber 116.

[0025] Electrically conductive material 120 may vary depending upon the intended use of the electrochromic device. For example, if the electrochromic device is a mirror, then the material may comprise a transparent conductive coating similar to electrically conductive material 118 (in which case a reflector is associated with rear surface 114B of second substrate 114). Alternatively, electrically conductive material 120 may comprise a layer of reflective material in accordance with the teachings of U.S. Patent No. 5,818,625. In this case, electrically conductive material 120 is associated with front surface 114A of second substrate 114. Typical coatings for this type of reflector include chromium, rhodium, ruthenium, silver, silver alloys, and combinations thereof.

[0026] Sealing member 122 may comprise any material that is capable of being adhesively bonded to the electrically conductive materials 118 and 120 to, in turn, seal chamber 116 so that electrochromic medium 124 does not inadvertently leak out of the chamber. As is shown in dashed lines in Fig. 1, it is also contemplated that the sealing member extend all the way to rear surface 112B and front surface 114A of their respective substrates. In such an embodiment, the layers of electrically conductive material 118 and 120 may be partially removed where the sealing member 122 is positioned. If electrically conductive materials 118 and 120 are not associated with their respective substrates, then

sealing member 122 preferably bonds well to glass. It will be understood that sealing member 122 can be fabricated from any one of a number of materials including, for example, those disclosed in U.S. Patent Nos. 4,297,401; 4,418,102; 4,695,490; 5,596,023; 5,596,024; and 6,157,480 entitled "Improved Seal For Electrochromic Devices," all of which are hereby
5 incorporated herein by reference in their entirety.

[0027] For purposes of the present disclosure, electrochromic medium 124 generally comprises an anodic material, a cathodic material, and a color-stabilizing additive dissolved in at least one solvent. During normal operation of device 100, the color-stabilizing additive enables the electrochromic medium 124 to remain colorless or nearly colorless in the high
10 transmission state. Typically both of the anodic and cathodic materials are electroactive and at least one of them is electrochromic. Regardless of its ordinary meaning, the term "electroactive" will be defined herein as a material that undergoes a modification in its oxidation state upon exposure to a particular electrical potential difference. Additionally, the term "electrochromic" will be defined herein, regardless of its ordinary meaning, as a material
15 that has a change in its extinction coefficient at one or more wavelengths upon exposure to a particular electrical potential difference. The medium is preferably chosen from the following categories:

[0028] (i) Single layer-single phase:

[0029] The electrochromic medium may comprise a single layer of material which
20 may include small non-homogenous regions and includes solution phase devices where a material is contained in solution in the ionically conducting electrolyte which remains in solution in the electrolyte when electrochemically oxidized or reduced. Solution phase electroactive materials may be contained in the continuous solution phase of a free standing rigid matrix in accordance with the teachings of U.S. Patent No. 5,928,572, entitled

"Electrochromic Layer And Devices Comprising Same" and U.S. Patent No. 5,910,854 entitled "Electrochromic Polymeric Solid Films, Manufacturing Electrochromic Devices Using Such Solid Films, And Processes For Making Such Solid Films And Devices," both of which are hereby incorporated herein by reference in their entirety.

5 [0030] More than one anodic and cathodic material can be combined to give a pre-selected color as described in U.S. Pat. No. 6,020,987 entitled "Improved Electrochromic Medium Capable of Producing A Pre-Selected Color," which is hereby incorporated herein by reference in its entirety.

[0031] The anodic and cathodic materials can be combined or linked by a bridging
10 unit as described in U.S. Patent No. 6,241,916 entitled "Electrochromic System," which is also hereby incorporated herein by reference in its entirety.

[0032] It is further possible to link anodic materials or cathodic materials by similar methods. The concepts described in these applications can further be combined to yield a variety of electroactive materials that are linked, including linking of an additive to an anodic
15 and/or cathodic material.

[0033] Additionally a single layer-single phase medium may include a medium where the anodic and cathodic materials are incorporated into a polymer matrix as is described in International Application Serial No. PCT/WO99/02621 entitled "Electrochromic Polymer System" and the previously referenced and incorporated '854 patent.

20 [0034] (ii) Multilayer – the medium may be made up in layers and includes a material attached directly to an electrically conducting electrode or confined in close proximity thereto which remains attached or confined when electrochemically oxidized or reduced. Examples of this type of electrochromic medium include a WO₃/ionically conducting layer/counter layer electrochromic medium. An organic or organometallic layer

attached to the electrode may also be included in this type.

[0035] (iii) Multiphase – one or more materials in the medium undergoes a change in phase during the operation of the device, for example a material contained in solution in the ionically conducting electrolyte forms a layer on the electrically conducting electrode when electrochemically oxidized or reduced.

[0036] The cathodic material may include, for example, viologens, such as methyl viologen tetrafluoroborate, octyl viologen tetrafluoroborate, or 1,1'3,3'-tetramethyl-4,4'-bipyridinium tetrafluoroborate. It will be understood that the preparation and/or commercial availability for each of the above-identified cathodic materials is well known in the art.

While specific cathodic materials have been provided, for illustrative purposes only, numerous other conventional cathodic materials are likewise contemplated for use including, but by no means limited to, those disclosed in U.S. Patent No. 4,902,108, which is hereby incorporated herein by reference in its entirety. Indeed, the only contemplated limitation relative to the cathodic material is that it should not adversely affect the electrochromic performance of the device 100. Moreover, it is contemplated that the cathodic material may comprise a solid transition metal oxide, including, but not limited to, tungsten oxide.

[0037] The anodic material may comprise any one of a number of materials including ferrocene, substituted ferrocenes, substituted ferrocenyl salts, phenazine, substituted phenazines, phenothiazine, substituted phenothiazines, thianthrene, or substituted thianthrenes. Examples of anodic materials may include di-tert-butyl-diethylferrocene, (6-(tetra-tert-butylferrocenyl)hexyl)triethylammonium tetrafluoroborate, (3-(tetra-tert-butylferrocenyl)propyl)triethylammonium tetrafluoroborate, 3,7,10-trimethylphenothiazine, 2,3,7,8-tetramethoxythianthrene, 10-methylphenothiazine, and 5,10-dimethylphenazine. It will be understood that numerous other anodic materials are contemplated for use including

those disclosed in the previously referenced and incorporated '108 patent as well as the previously referenced and incorporated '505 patent.

[0038] For illustrative purposes only, the concentration of the anodic and cathodic materials can range from approximately 1mM to approximately 500mM and more preferably from approximately 5mM to approximately 50mM. While particular concentrations of the anodic as well as cathodic materials have been provided, it will be understood that the desired concentration may vary greatly depending upon the geometric configuration of the chamber containing electrochromic medium 124.

[0039] For purposes of the present disclosure, the solvent of electrochromic medium 124 may comprise any one of a number of common, commercially available solvents including 3-methylsulfolane, glutaronitrile, dimethyl sulfoxide, dimethyl formamide, acetonitrile, tetraglyme and other polyethers, alcohols such as ethoxyethanol, nitriles, such as 3-hydroxypropionitrile, 2-methylglutaronitrile, ketones including 2-acetylbutyrolactone, cyclopentanone, cyclic esters including beta-propiolactone, gamma-butyrolactone, gamma-valerolactone, propylene carbonate, ethylene carbonate and homogenous mixtures of the same. While specific solvents have been disclosed as being associated with the electrochromic medium, numerous other solvents or plasticizers that would be known to those having ordinary skill in the art having the present disclosure before them are likewise contemplated for use.

[0040] In a first embodiment of the invention, the additive is more easily reduced than the cathodic material, and, during normal operation of the electrochromic device, serves to substantially preclude the formation of a residual reduced cathodic material while the device is in its high transmission state. The term "high transmission state" is defined as the bleached state, the unpowered state, the unactivated state and/or the open circuit state of the

electrochromic device, or a state where it is desirable for the electrochromic medium within the device to be colorless or nearly colorless. As previously discussed, a residual reduced cathodic material can form from any one of a number of different reasons, and can leave the electrochromic medium undesirably tinted or colored, when it is desirable for the electrochromic medium to be colorless or nearly colorless.

[0041] In this first embodiment of the invention, the additive may comprise an oxidized form of the anodic material, or alternatively, the additive may comprise an additional material (other than the anodic material) present in an oxidized form. Preferably, the additive comprises a redox potential between that of both the anodic and cathodic materials. For example, the additive may comprise one or more materials such as ferrocenium salts, substituted ferrocenium salts, phenazinium salts, and substituted phenazinium salts. Specific materials may include, for example, di-tert-butyl-diethylferrocenium tetrafluoroborate, (6-(tetra-tert-butylferrocenium)hexyl)triethylammonium di-tetrafluoroborate, (3-(tetra-tert-butylferrocenium)propyl)triethylammonium di-tetrafluoroborate, 5-methylphenazinium tetrafluoroborate. Preferably the concentration of the additive ranges from approximately 0.01mM to approximately 10mM.

[0042] In a second embodiment of the invention, the additive comprises a reduced form of the cathodic material, and, during normal operation of the electrochromic device, serves to substantially preclude the formation of a residual oxidized anodic material while the device is in its high transmission state. Examples of suitable cathodic materials and their associated reduced species may include, for example, those identified below:

Cathodic Material	Additive
$[\text{Ru}(\text{NH}_3)_6]^{3+}$	$[\text{Ru}(\text{NH}_3)_6]^{2+}$
$[\text{Fe}(\text{CN})_6]^{3-}$	$[\text{Fe}(\text{CN})_6]^{4-}$
$[\text{Cr}(\text{bpy}^*)_3]^{3+}$	$[\text{Cr}(\text{bpy}^*)_3]^{2+}$
$[\text{PMo}_{12}\text{O}_{40}]^{3-}$	$[\text{PMo}_{12}\text{O}_{40}]^{4-}$

* wherein bpy is a bipyridine based ligand

** wherein $\text{PMo}_{12}\text{O}_{40}$ is a polyoxometalate complex

5 It will be understood that only the electrochemically relevant portion of the complexes have been disclosed and that the above-identified complexes can be associated with any one of a number of cations or anions to form a neutral species. Preferably the concentration of the additive ranges from approximately 0.01mM to approximately 10mM.

[0043] In a third embodiment of the invention, the additive is more easily oxidized
10 than the anodic material and is preferably selected from one or more materials, such as substituted ferrocenes, substituted ferrocenyl salts, and mixtures thereof. During normal operation of the electrochromic device, the additives comprising the third embodiment serve to substantially preclude the formation of a residual oxidized anodic material while the device is in its high transmission state. Specific examples of suitable materials include di-tert-butyl-
15 diethylferrocene, (6-(tetra-tert-butylferrocenyl)hexyl)triethylammonium tetrafluoroborate, and (3-(tetra-tert-butylferrocenyl)propyl)triethylammonium tetrafluoroborate. While specific materials have been disclosed, for illustrative purposes only, numerous other materials that would be known to those having ordinary skill in the art having the present disclosure before them are likewise contemplated for use. Preferably the concentration of these additives
20 ranges from approximately 0.01mM to approximately 10mM.

[0044] In a fourth embodiment of the invention, the additive comprises a first component that is more easily reduced than the cathodic material and a second component that is more easily oxidized than the anodic material. During normal operation of the

electrochromic device, the first component serves to substantially preclude the formation of a residual reduced cathodic material and the second component serves to substantially preclude the formation of a residual oxidized anodic material while the device is in its high transmission state.

5 [0045] The first additive component may comprise either an oxidized form of the anodic material, or an additional electroactive material present in an oxidized form – or both with appropriate control of additive stoichiometry. Examples of suitable first components include ferrocinium salts, substituted ferrocinium salts, phenazinium salts, and substituted phenazinium salts. Specific materials may include, for example, di-tert-butyl-
10 diethylferrocinium tetrafluoroborate, (6-(tetra-tert-butylferrocinium)hexyl)triethylammonium di-tetrafluoroborate, (3-(tetra-tert-butylferrocinium)propyl)triethylammonium di-tetrafluoroborate, and 5-methylphenazinium tetrafluoroborate.

[0046] The second additive component may comprise one or more materials, such as substituted phenazines, substituted ferrocenes, substituted ferrocenyl salts, and mixtures
15 thereof. Specific materials may include, for example, 5-methylphenazine, (6-(tetra-tert-butylferrocenyl)hexyl)triethylammonium tetrafluoroborate, (3-(tetra-tert-butylferrocenyl)propyl)triethylammonium tetrafluoroborate, di-tert-butyl-diethylferrocene, and mixtures thereof. Preferably the concentration of both the first and second components each ranges from approximately 0.01mM to approximately 10mM.

20 [0047] In addition, the electrochromic medium may also comprise other materials, such as light absorbers, light stabilizers, thermal stabilizers, antioxidants, viscosity modifiers including thickeners, and/or tint providing agents. Suitable UV-stabilizers may include: the material ethyl-2-cyano-3,3-diphenyl acrylate, sold by BASF of Parsippany, NY, under the trademark Uvinul N-35 and by Aceto Corp., of Flushing, NY, under the trademark Viosorb

910; the material (2-ethylhexyl)-2-cyano-3,3-diphenyl acrylate, sold by BASF under the trademark Uvinul N-539; the material 2-(2'-hydroxy-4'-methylphenyl)benzotriazole, sold by Ciba-Geigy Corp. under the trademark Tinuvin P; the material 2-hydroxy-4-methoxybenzophenone sold by American Cyanamid under the trademark Cyasorb UV 9; and the material 2-ethyl-2'-ethoxyalanilide sold by Sandoz Color & Chemicals under the trademark Sanduvor VSU – to name a few. Thickeners include polymethylmethacrylate (PMMA) which is commercially available from, among other chemical suppliers, Aldrich Chemical Co.

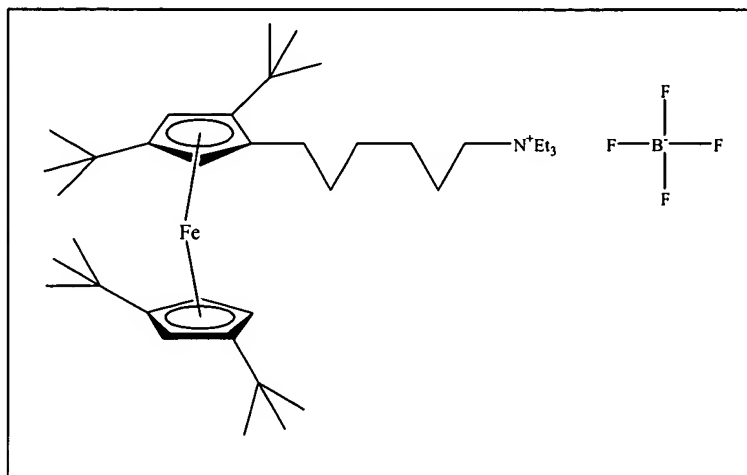
[0048] It will be understood that during normal operation, the electrochromic devices of the present invention are intended to be cycled between a high transmission state and a low transmission state numerous times while maintaining a colorless or nearly colorless electrochromic medium during the high transmission state relative to an electrochromic medium without the additive.

[0049] Electrochromic devices having as a component part a color-stabilized electrochromic medium can be used in a wide variety of applications wherein the transmitted or reflected light can be modulated. Such devices include rear-view mirrors for vehicles; windows for the exterior of a building, home or vehicle; skylights for buildings including tubular light filters; windows in office or room partitions; display devices; contrast enhancement filters for displays; light filters for photographic devices and light sensors; and indicators for power cells as well as primary and secondary electrochemical cells.

[0050] The electrochromic media of the present invention utilize many different materials. The preparation and/or commercially available sources are provided herein, unless the material is well known in the art. It will be understood that, unless specified otherwise, the starting reagents are commercially available from Aldrich Chemical Co., Milwaukee, WI,

or other common chemical suppliers. It will be understood that conventional chemical abbreviations will be used when appropriate including the following: grams (g); milliliters (ml); moles (mol), millimoles (mmol), molar (M), and millimolar (mM).

Synthesis of (6-(tetra-tert-butylferrocenyl)hexyl)triethylammonium tetrafluoroborate



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[0051] The synthesis of (6-(tetra-tert-butylferrocenyl)hexyl)triethylammonium tetrafluoroborate is a three step synthesis. First, 6-bromo-1-(tetra-tert-butylferrocenyl)-2-hexanone is prepared. Second, the ketonic product is converted to 6-bromo-1-(tetra-tert-butylferrocenyl)hexane, which in turn, is subsequently converted into (6-(tetra-tertbutylferrocenyl)hexyl)triethyl-ammonium tetrafluoroborate.

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Preparation of 6-bromo-1-(tetra-tert-butylferrocenyl)-2-hexanone

[0052] First, a nitrogen purged flask was charged with 350ml of dichloroethane, 50.0g (122mmol) of tetra-tert-butylferrocene (prepared according to T. Leigh, J. Am. Chem. Soc. 1964, 3294-3302), and 19.3ml (126mmol) of 6-bromohexanoyl chloride. Second, the solution was cooled to 0 degrees centigrade, whereupon 13.3g (100mmol) of AlCl_3 was charged into the reaction vessel in 3 equal portions at two hour intervals. It will be understood that the freshness and/or purity of the AlCl_3 can impact the degree of substitution

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of, for example, tert-butyl groups on a cyclopentadienyl ligand. Third, the reaction mixture was then slowly poured into 300ml of agitating H₂O. Fourth, the organic-aqueous mixture was charged with a sufficient quantity of diethyl ether so that an organic layer was appreciably formed on top of the aqueous layer. Fifth, 50ml of concentrated hydrochloric acid (HCl) was charged into the vessel. Sixth, approximately 2-5g of zinc dust was charged into the vessel to reduce any ferrocenium species present in the aqueous layer to the ether soluble ferrocene. Once the layers were clearly defined, they were separated and the aqueous layer was extracted with 200 ml of diethyl ether (Et₂O). The two organic portions were combined and washed with NaHCO₃ and brine. Next the organic solution was dried over MgSO₄. The organic solution was then decanted from the MgSO₄ and filtered. Next, the solvent was removed by rotary evaporation to yield a red oil. The red oil was applied to a vacuum assisted silica gel column and washed with hexane to remove any residual ferrocene. The product was eluted with Et₂O. Upon solvent removal and cooling in a freezer, 64.29g of 6-bromo-1-(tetra-tert-butylferrocenyl)-2-hexanone was isolated as a red solid.

Preparation of 6-bromo-1-(tetra-tert-butylferrocenyl)hexane

[0053] First, 2.27g (17.02mmol) of AlCl₃ was dissolved in 200ml of dry Et₂O in a Schlenk flask under controlled, positive nitrogen pressure. Second, the solution was cooled to 0 degrees centigrade and 17.0g (17.0mmol) of 1.0M LiAlH₄ was charged into the flask via syringe. The resulting suspension was warmed to room temperature and agitated for approximately 15 minutes. Next, 10.00g (17.02mmol) of the above prepared 6-bromo-1-(tetra-tert-butylferrocenyl)-2-hexanone was slowly added to the suspension. Once the addition of the ketonic product was complete, the solution was heated to reflux for approximately 3 hours, after which time the solution was cooled to room temperature. The reaction was then quenched by slowly adding H₂O to the solution. When no further

exothermic reaction was observed, 250ml of H₂O was added to dilute the solution. The solution was then transferred to a separatory funnel, whereupon the organic layer was collected and the aqueous layer was extracted with 100ml of Et₂O. The organic portions were combined and then washed with NaHCO₃ and brine. Next, the solution was dried over
5 MgSO₄. The solution was then decanted from the drying agent and filtered. Next, the solvent was removed via rotary evaporation yielding a yellow-orange oil. The oil was dissolved in a small amount of hexane, applied to a vacuum assisted gel column, and eluted with more hexane. Upon solvent removal, 8.73g of 6-bromo-1-(tetra-tert-butylferrocenyl)hexane was isolated as a yellow-orange solid.

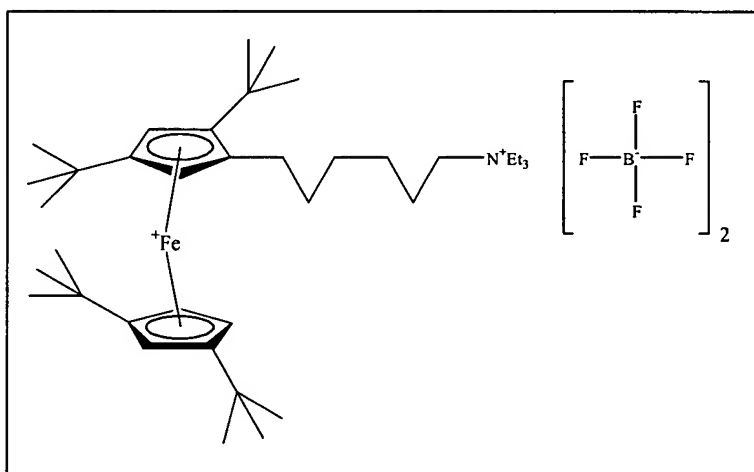
10 Preparation of (6-(tetra-tert-butylferrocenyl)hexyl)triethylammonium tetrafluoroborate

[0054] First, 87.5ml (628mmol) of triethylamine (NEt₃), and 53.1g (92.6mmol) of 6-bromo-1-(tetra-tert-butylferrocenyl)hexane, and 50ml of acetonitrile were charged into a reaction vessel. The solution was then heated to reflux for 4 days. During this time the reaction was periodically monitored by thin layer chromatography (TLC), using hexane as the
15 eluent, for the disappearance of the starting material. After cooling to room temperature, the solvent was removed by rotary evaporation and the product was precipitated by addition of Et₂O. The bromide salt of the product was collected on a filter frit, and washed with several portions of cold Et₂O. Next, the salt was dried *in vacuo* to yield an orange solid. An anion exchange was then performed by dissolving NaBF₄ in water and subsequently removing
20 residual solid particles via filtration. Next the bromide salt of the product was dissolved in Methanol (MeOH) and the NaBF₄ dissolved in water was added to the bromide salt solution. The methanol was slowly removed via rotary evaporation until the product began to precipitate. The orange precipitate was collected on a filter frit, and the recrystallization process was repeated. Finally the precipitate was dissolved in a minimum amount of MeOH,

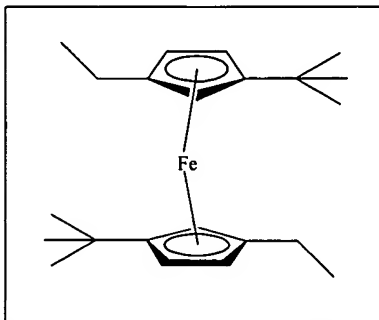
and Et₂O was added slowly to precipitate (6-(tetra-tert-butylferrocenyl)hexyl)triethylammonium tetrafluoroborate, an orange solid, which was collected on a frit, dried *in vacuo*, and stored for later use.

[0055] It will be understood that shorter and longer alkyl chain substituted groups, such as a propyl alkyl chain derivative can likewise be synthesized using shorter or longer alkyl chain precursor reagents.

Synthesis of (6-(tetra-tert-butylferrocenium)hexyl)triethylammonium di-tetrafluoroborate



[0056] First, 10.00g (14.67mmol) of the above-prepared (6-(tetra-tert-butylferrocenyl)-hexyl)triethylammonium tetrafluoroborate was dissolved in 150ml of dichloromethane (CH₂Cl₂). Next 5.0g (25.7mmol) of AgBF₄ was added in 2 equal portions at a 5 minute interval. After agitating for 30 minutes, the solution was filtered and the solvent was removed by rotary evaporation, yielding a green solid. The green solid was redissolved in a minimal amount of CH₂Cl₂ and the product was precipitated by the addition of Et₂O. The solid was dried *in vacuo* to yield 10.57g of (6-(tetra-tert-butylferrocenium)hexyl)-triethylammonium di-tetrafluoroborate as a dark green, crystalline solid.

Synthesis of Di-tert-butyl-diethylferrocene

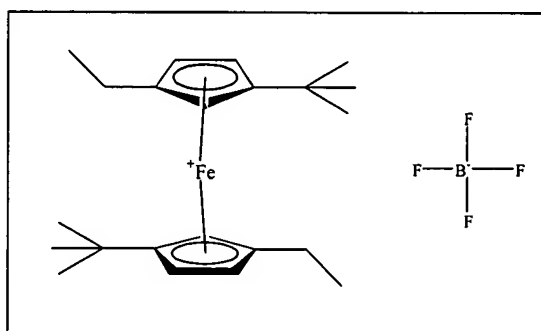
[0057] First, a reaction flask was thoroughly purged with nitrogen and charged with 300ml of dichloroethane, 10.0g (33.53mmol) of di-tert-butylferrocene (prepared according to T. Leigh, J. Am. Chem. Soc. 1964, 3294-3302), and 7.44ml (100.6mmol) of freshly distilled acetyl bromide. The solution was agitated, cooled to 0 degrees centigrade, and charged with 8.94g (67.06mmol) of AlCl_3 . The solution was held at 0 degrees centigrade for one hour and then warmed to room temperature. Agitation was maintained throughout the holding and warming periods. The reaction mixture was then transferred into a beaker containing a mixture of agitating ice and dilute HCl. Next, Et_2O was added to form an organic layer on top of the aqueous layer. The organic layer was separated – via separatory funnel and the aqueous layer was extracted with 200ml of Et_2O . The organic portions were combined and washed with NaHCO_3 and brine and then dried over MgSO_4 . Next, the solution was decanted from the MgSO_4 and placed on a rotary evaporator to remove the solvent, which yielded a red oil. The red oil was applied to a silica gel column and washed with hexane to strip any residual starting material from the product. The ketonic product was then eluted with a mixture of ethyl acetate (EtOAc)/hexane (30:70 by vol.) Upon solvent removal, 5.55g of di-tert-butyl-diacetylferrocene was collected.

[0058] After the di-tert-butyl-diacetylferrocene was prepared, a Schlenk flask under

positive nitrogen pressure was charged with 25ml of dry Et₂O. Second 0.35g (2.61mmol) of AlCl₃ was charged into the reaction flask. Agitation was initiated and the AlCl₃ dissolved into solution. Third, 5.23ml (5.23mmol) of 1M LiAlH₄ in Et₂O was charged into the reaction flask via syringe. The resulting suspension was agitated for approximately 15 minutes.

5 Fourth, 1.00g (2.62mmol) of the above-prepared di-tert-butyl-diacetylferrocene was slowly charged into the reaction vessel. Next, the solution was heated to reflux for approximately 3 hours and then cooled to room temperature overnight with continuous agitation. The reaction was then quenched by the slow addition of wet Et₂O to the solution. The organic layer was separated from the aqueous layer – via separatory funnel. Next, the aqueous layer was
 10 extracted with 100ml of Et₂O. The organic portions were combined and washed with H₂O and brine, which was followed by drying over MgSO₄. The solution was decanted from the drying agent and filtered. Next the solvent was stripped via rotary evaporation, which yielded a yellow-orange oil. The oil was dissolved in a small amount of hexane, applied to a vacuum assisted silica gel column, and eluted with more hexane. Upon solvent removal, 0.627g of di-
 15 tert-butyl-diethylferrocene was collected and stored for later use.

Synthesis of Di-tert-butyl-diethylferroceninium tetrafluoroborate



[0059] First, 0.50g (1.41mmol) of the above-prepared di-tert-butyl-diethylferrocene, 20ml of CH₂Cl₂, and 0.282g (1.45mmol) of AgBF₄ were charged into a reaction vessel,

whereupon agitation was initiated. After approximately 2 hours of agitation, the solution was filtered and the solvent was removed by rotary evaporation, yielding a green solid. The green solid was recrystallized by layered, solvent diffusion of Et₂O into a concentrated solution of crude di-tert-butyl-diethylferrocenium BF₄ in CH₂Cl₂. The solid was dried under vacuum to
5 yield 0.51 g of di-tert-butyl-diethylferrocenium BF₄ as a dark green, crystalline solid.

[0060] In support of the present invention, several experiments were conducted wherein electrochromic devices were prepared which comprised a color-stabilizing additive, the color-stabilized performance of which were compared to analogous devices fabricated without a color-stabilizing additive.

10 [0061] In discussing colors it is useful to refer to the Commission Internationale de l'Eclairage's (CIE) 1976 CIELAB Chromaticity Diagram (commonly referred to as the L*a*b* chart). The technology of color is relatively complex, but a fairly comprehensive discussion is given by F. W. Billmeyer and M. Saltzman in the Principles of Color Technology, 2nd Ed., J. Wiley and Sons Inc. (1981), and the present disclosure, as it relates to
15 color technology and terminology, generally follows that discussion. On the L*a*b* chart, L* defines lightness, a* denotes the red/green value, and b* denotes the yellow/blue value. Each of the electrochromic media has an absorption spectra at each particular voltage that may be converted into a three number designation, their L*a*b* values. For the present discussion, the a*, b*, ΔE, and ΔY values are relevant inasmuch as: (1) a medium with an
20 increased a* value is more red; (2) a medium with a decreased a* value is more green; (3) a medium with an increased b* value is more yellow; (4) a medium with a decreased b* value is more blue; (5) a medium with an increased ΔE value has a greater overall color change; and (6) a medium with an increased ΔY value has a great overall change in lightness and/or intensity.

[0062] The Δa^* , Δb^* , ΔE , and ΔY values are calculated by importing $L^*a^*b^*$ values into the following formulae:

$$\Delta a^* = (a_t^* - a_0^*)$$

wherein : Subscript "0" is an initial value; and
: Subscript "t" is a value after a given amount of time

$$\Delta b^* = (b_t^* - b_0^*)$$

wherein : Subscript "0" is an initial value; and
: Subscript "t" is a value after a given amount of time

$$\Delta E = \text{SQRT}((L_t^* - L_0^*)^2 + (a_t^* - a_0^*)^2 + (b_t^* - b_0^*)^2)$$

wherein : SQRT is the square root operation;
: Subscript "0" is an initial value (for L^* , a^* , and b^*); and
: Subscript "t" is a value after a given amount of time (for L^* , a^* , and b^*)

$$\Delta Y = 100 \times ((L_t^* + 16)/116)^3 - ((L_0^* + 16)/116)^3$$

wherein : Subscript "0" is an initial value; and
: Subscript "t" is a value after a given amount of time.

[0063] It will be understood that in each of the experiments provided below, the electrochromic materials were dissolved in propylene carbonate (PC).

Experiment No. 1

[0064] In this experiment two electrochromic media were prepared by mixing the following materials together in the concentrations provided below:

Experiment No. 1A

Component	Material	Concentration
Cathodic	Octylviologen BF_4	34.0mM
Anodic	5,10-Dimethylphenazine	26.5mM
Additive	None	-
UV-Stabilizer	T-butylpentylester of Tinuvin P*	50.0mM
UV-Stabilizer	Tinuvin P	30.0mM
Thickener	PMMA	3 % by wt.

* a.k.a. 3-[3-(2H-benzotriazole-2-yl)-5-(1,1-dimethylethyl)-4-hydroxyphenyl]propionic acid pentyl ester

Experiment No.1B

Component	Material	Concentration
Cathodic	Octylviologen BF ₄	34.0mM
Anodic	5,10-Dimethylphenazine	26.5mM
Additive	(6-(tetra-tert-butylferrocenyl)hexyl)triethylammonium BF ₄	5.0mM
UV-Stabilizer	T-butylpentylester of Tinuvin P	50.0mM
UV-Stabilizer	Tinuvin P	30.0mM
Thickener	PMMA	3 % by wt.

[0065] Each of the media were associated with an electrochromic mirror for testing.

Specifically, the mirror comprised two 2x5 inch substrates. The first substrate was coated with generally clear, conductive fluorine doped tin oxide, and the second was coated with fluorine doped tin oxide with a silver reflector on rear surface 114B. The substrates were spaced 137 microns apart for accommodating the medium.

[0066] As can be seen, Experiment No. 1A does not include an additive and Experiment No. 1B comprises (6-(tetra-tert-butylferrocenyl)hexyl)triethylammonium BF₄ as an additive. In order to simulate a harsh oxidative environment, each of the above-prepared media were placed into a conventional autoclave with an oxygen input line at 400 p.s.i. at ambient temperature. The media were then evaluated for their color stability by obtaining L*a*b* values at predetermined intervals. The L*a*b* data for Experiment Nos. 1A and 1B are provided below.

Experiment No. 1 – Autoclave

Experiment 1A						Experiment 1B					
Hours	L*	a*	b*	ΔE	ΔY	Hours	L*	a*	b*	ΔE	ΔY
0	88.93	-5.25	8.59	0.00	0.00	0	89.22	-4.78	9.35	0.00	0.00
168	89.25	-5.44	8.64	0.38	0.68	168	89.52	-4.90	9.30	0.33	0.64
336	89.07	-5.97	9.85	1.46	0.30	336	89.31	-5.04	9.69	0.44	0.19
504	88.94	-6.49	11.18	2.87	0.02	504	89.00	-5.27	10.44	1.22	0.47
672	88.39	-7.44	14.11	5.96	1.14	672	88.81	-5.82	12.25	3.11	0.87
840	87.72	-8.34	17.76	9.75	2.53	840	88.48	-6.47	14.87	5.82	1.56
1008	87.41	-8.37	19.06	11.03	3.17	1008	88.41	-6.40	15.38	6.30	1.71
1176	87.10	-8.84	20.99	13.04	3.81	1176	88.26	-6.44	16.09	7.01	2.02
1344	86.90	-8.44	21.29	13.25	4.21	1344	87.96	-6.34	16.40	7.33	2.65
1512	86.57	-8.44	22.20	14.18	4.88	1512	87.66	-6.40	16.92	7.90	3.27
1680	86.20	-8.44	23.58	15.57	5.63	1680	87.17	-6.81	18.49	9.58	4.28
1848	85.53	-8.97	25.68	17.82	6.96	1848	87.01	-6.79	19.11	10.21	4.60
2016	84.84	-10.01	28.97	21.32	8.32	2016	86.61	-6.67	19.47	10.62	5.42

[0067] The medium without the additive turned substantially more green, which is shown in Fig. 2 as an increasing negative a^* value, in Fig. 3 as an increasing b^* value, and as an overall color change in the significantly increased ΔE value. Therefore, Experiment No. 1

5 verifies that, indeed, the usage of the above-identified additive provides an effective mechanism to minimize the adverse coloration effects associated with oxidative environments.

Experiment No. 2

[0068] In this experiment four electrochromic media were prepared by mixing the

10 following materials together in the concentrations provided below:

Experiment No. 2A

Component	Material	Concentration
Cathodic	Octylviologen BF_4	34.0mM
Anodic	3,7,10-trimethylphenothiazine	26.5mM
Additive	None	-
UV-Stabilizer	Tinuvin P	30.0mM
Thickener	PMMA	3 % by wt.

Experiment No. 2B

Component	Material	Concentration
Cathodic	Octylviologen BF_4	34.0mM
Anodic	3,7,10-trimethylphenothiazine	26.5mM
Additive	(6-(tetra-tert-butylferrocenyl)hexyl)triethylammonium BF_4	2.0mM
UV-Stabilizer	Tinuvin P	30.0mM
Thickener	PMMA	3 % by wt.

Experiment No. 2C

Component	Material	Concentration
Cathodic	Octylviologen BF_4	34.0mM
Anodic	3,7,10-trimethylphenothiazine	26.5mM
Additive	(6-(tetra-tert-butylferrocenyl)hexyl)triethylammonium $(\text{BF}_4)_2$	2.0mM
UV-Stabilizer	Tinuvin P	30.0mM
Thickener	PMMA	3 % by wt.

Experiment No. 2D

Component	Material	Concentration
Cathodic	Octylviologen BF_4	34.0mM
Anodic	3,7,10-trimethylphenothiazine	26.5mM
First Additive	(6-(tetra-tert-butylferrocenyl)hexyl)triethylammonium BF_4	2.0mM
Second Additive	(6-(tetra-tert-butylferrocenyl)hexyl)triethylammonium $(\text{BF}_4)_2$	2.0mM
UV-Stabilizer	Tinuvin P	30.0mM
Thickener	PMMA	3 % by wt.

[0069] As can be seen, Experiment No. 2A does not include an additive and Experiment Nos. 2B-2D comprise different ferrocene complexes as additives. Each of the media (2A-2D) were associated with an electrochromic mirror similar in construction to those described in Experiment No. 1 for color stabilization testing. Duplicate sets of mirrors were constructed, half of which were placed in an autoclave under the same conditions identified in Experiment No. 1, while the other half were stored at 85 degrees centigrade to simulate exposure to prolonged elevated temperatures. The L*a*b* data was collected at predetermined intervals, which is provided below.

Experiment No. 2 – Autoclave

Experiment 2A						Experiment 2B					
Hours	L*	a*	b*	ΔE	ΔY	Hours	L*	a*	b*	ΔE	ΔY
0	88.44	-3.45	7.76	0.00	0.00	0	88.80	-3.54	7.81	0.00	0.00
168	88.81	-3.46	7.67	0.38	0.78	168	88.93	-3.62	7.70	0.19	0.27
336	88.67	-3.63	8.19	0.52	0.48	336	88.80	-3.73	7.78	0.19	0.00
504	88.62	-3.49	8.28	0.55	0.38	504	88.90	-4.00	7.70	0.48	0.21
672	87.86	-3.75	9.82	2.16	1.21	672	88.75	-4.25	7.83	0.71	0.11
840	86.76	-3.35	10.94	3.60	3.47	840	88.28	-4.21	8.20	0.93	1.09
1008	86.45	-3.31	12.04	4.72	4.09	1008	88.04	-4.53	8.89	1.65	1.59
1176	86.33	-3.92	13.45	6.09	4.33	1176	87.78	-4.96	10.07	2.86	2.13
1344	86.01	-4.03	14.76	7.43	4.98	1344	87.80	-5.59	12.30	5.04	2.09
1512	85.71	-4.10	15.67	8.39	5.57	1512	87.40	-5.82	13.93	6.68	2.92
1680	84.64	-2.99	15.62	8.74	7.68	1680	87.41	-6.12	14.96	7.73	2.90
1848	83.59	-1.68	15.15	9.01	9.70	1848	87.21	-6.39	16.33	9.12	3.31
2016	82.44	0.08	14.36	9.59	11.87	2016	87.13	-6.77	17.93	10.75	3.47
2184	81.42	0.75	14.09	10.34	13.75	2184	86.95	-6.82	18.79	11.61	3.84
2352	80.99	2.00	13.55	10.90	14.53	2352	86.58	-6.42	18.89	11.66	4.59
Experiment 2C						Experiment 2D					
Hours	L*	a*	b*	ΔE	ΔY	Hours	L*	a*	b*	ΔE	ΔY
0	88.16	-4.35	8.16	0.00	0.00	0	88.38	-3.96	8.15	0.00	0.00
168	88.50	-4.46	8.26	0.37	0.71	168	88.51	-3.87	7.95	0.25	0.27
336	88.15	-4.46	8.51	0.37	0.02	336	88.00	-3.82	7.94	0.46	0.79
504	88.06	-4.50	8.86	0.72	0.21	504	88.40	-3.90	7.93	0.23	0.04
672	87.46	-4.76	9.83	1.86	1.45	672	87.67	-4.09	8.66	0.88	1.48
840	86.98	-4.88	10.87	3.00	2.43	840	87.15	-3.98	9.26	1.66	2.55
1008	86.71	-5.15	11.92	4.11	2.98	1008	87.00	-4.07	10.02	2.33	2.85
1176	86.51	-5.54	13.25	5.48	3.39	1176	86.47	-4.23	11.34	3.73	3.93
1344	85.61	-4.45	13.02	5.49	5.19	1344	86.17	-4.35	12.60	4.98	4.53
1512	84.66	-3.16	12.62	5.79	7.06	1512	85.93	-4.53	13.63	6.03	5.01
1680	82.30	-0.54	11.50	7.75	11.54	1680	85.45	-4.77	14.32	6.88	5.96
1848	81.94	0.51	11.28	8.49	12.21	1848	85.93	-5.21	15.21	7.58	5.01

2016	80.37	2.30	10.63	10.54	15.06	2016	85.96	-5.60	16.31	8.67	4.95
2184	80.33	2.72	10.73	10.86	15.13	2184	85.90	-5.74	17.25	9.60	5.07
2352	79.46	3.91	10.46	12.22	16.67	2352	86.05	-5.81	17.61	9.92	4.77

Experiment No. 2 – Thermal

Experiment 2A						Experiment 2B					
Hours	L*	a*	b*	ΔE	ΔY	Hours	L*	a*	b*	ΔE	ΔY
0	88.30	-3.86	8.67	0.00	0.00	0	88.55	-3.98	8.49	0.00	0.00
167	87.34	-3.81	6.99	1.94	1.99	167	86.76	-4.41	6.15	2.98	3.69
314	83.04	-5.69	1.29	9.25	10.45	314	82.74	-6.25	0.72	9.96	11.54
478	79.62	-6.73	-2.58	10.98	16.68	478	81.28	-6.65	-1.07	12.30	14.23
651	77.62	-7.54	-5.35	18.00	20.12	651	80.37	-7.06	-2.23	13.83	15.87
840	77.43	-7.30	-5.58	18.25	20.44	840	81.15	-6.63	-1.07	12.38	14.47
1025	75.06	-8.05	-8.39	22.00	24.32	1025	80.54	-6.91	-1.35	13.02	15.57
1193	75.34	-7.86	-7.75	21.30	23.87	1193	80.53	-6.78	-1.37	13.01	15.58
1375	75.65	-8.24	-7.41	20.92	23.37	1375	80.03	-7.06	-1.98	13.85	16.48
1543	74.97	-7.98	-8.44	22.08	24.46	1543	79.88	-6.92	-2.29	14.14	16.74
1785	74.44	-7.93	-8.74	22.62	25.30	1785	79.75	-6.98	-2.22	14.18	16.97
1972	74.28	-8.06	-8.19	22.33	25.55	1972	78.95	-7.27	-3.07	15.38	18.37
2261	74.94	-7.56	-8.03	21.70	24.51	2261	79.17	-7.03	-2.95	15.10	17.99
Experiment 2C						Experiment 2D					
Hours	L*	a*	b*	ΔE	ΔY	Hours	L*	a*	b*	ΔE	ΔY
0	87.88	-5.15	9.26	0.00	0.00	0	88.26	-4.46	8.73	0.00	0.00
167	88.04	-4.34	8.16	1.38	0.33	167	88.35	-4.05	8.17	0.70	0.19
314	88.06	-4.21	8.11	1.50	0.37	314	88.28	-3.91	8.09	0.84	0.04
478	87.98	-4.11	8.02	1.62	0.20	478	88.20	-3.92	7.97	0.93	0.13
651	87.94	-4.03	8.06	1.64	0.12	651	88.06	-3.96	7.80	1.07	0.42
840	87.86	-3.94	7.94	1.79	0.05	840	87.68	-4.06	7.41	1.50	1.21
1025	87.80	-3.88	8.19	1.66	0.17	1025	87.26	-4.26	7.03	1.98	2.07
1193	87.76	-3.92	8.19	1.63	0.25	1193	87.07	-4.42	6.79	2.28	2.46
1375	87.81	-3.90	8.29	1.58	0.15	1375	86.49	-4.61	6.32	2.99	3.64
1543	87.72	-3.83	8.12	1.75	0.34	1543	86.54	-4.57	6.10	3.14	3.54
1785	87.61	-3.87	8.15	1.72	0.56	1785	86.28	-4.59	6.10	3.29	4.06
1972	87.63	-3.82	8.23	1.70	0.52	1972	86.16	-4.87	5.72	3.69	4.30
2261	87.58	-3.74	8.06	1.88	0.62	2261	85.86	-4.56	5.75	3.83	4.90

[0070] In reference to the autoclave experiment, Fig. 4 depicts that the media without
5 the ferrocenyl additive (Autoclave Exp. 2A, 2C) turned more red (the positive a* value) than
the media with the ferrocenyl additive (Autoclave Exp. 2B-2D). Fig. 5 graphically indicates
the b* values for the media that were associated with mirrors stored at an elevated
temperature (Thermal Exp. 2A-2D). In particular, the media comprising a ferrocenium
additive (Thermal Exp. 2C, 2D) did not appreciably decrease in b* value. In comparison, the

media without the ferrocinium additive began to "fail" or turn blue almost immediately.

[0071] In addition, Figs. 4 and 5 collectively demonstrate that a medium comprising both ferrocenyl as well as ferrocinium species maintains relatively constant a^* and b^* values in both oxidative and prolonged elevated temperature environments.

5

Experiment No. 3

[0072] In this experiment two electrochromic media were prepared by mixing the following materials together in the concentrations provided below:

Experiment No. 3A

Component	Material	Concentration
Cathodic	Methylviologen BF_4	34.0mM
Anodic	(6-(tetra-tert-butylferrocenyl)hexyl)triethylammonium BF_4	21.8mM
Additive	None	-
UV-Stabilizer	T-butylpentylester of Tinuvin P	50.0mM
UV-Stabilizer	Tinuvin P	30.0mM
Thickener	PMMA	3 % by wt.

10

Experiment No. 3B

Component	Material	Concentration
Cathodic	Methylviologen BF_4	34.0mM
Anodic	(6-(tetra-tert-butylferrocenyl)hexyl)triethylammonium BF_4	21.8mM
Additive	(6-(tetra-tert-butylferrocinium)hexyl)triethylammonium $(\text{BF}_4)_2$	2.0mM
UV-Stabilizer	T-butylpentylester of Tinuvin P	50.0mM
UV-Stabilizer	Tinuvin P	30.0mM
Thickener	PMMA	3 % by wt.

[0073] As can be seen, Experiment No. 3A does not include an additive and Experiment No. 3B comprises (6-(tetra-tert-butylferrocinium)hexyl)triethyl-ammonium $(\text{BF}_4)_2$ as an additive. The media from Experiments 3A and 3B were placed into electrochromic windows comprising two 2x5 inch substrates. The first and second substrates were coated with generally clear, conductive fluorine doped tin oxide. The substrates were spaced 250 microns apart for accommodating the medium. The windows were stored at 85 degrees centigrade to simulate exposure to prolonged elevated temperatures and $L^*a^*b^*$ data was collected at predetermined intervals, which is provided below.

20

Experiment No. 3 – Thermal

Experiment 3A						Experiment 3B					
Hours	L*	a*	b*	ΔE	ΔY	Hours	L*	a*	b*	ΔE	ΔY
0	81.15	-4.01	19.45	0.00	0.00	0	80.28	-5.44	19.85	0.00	0.00
267	81.18	-3.71	19.60	0.34	0.06	267	80.33	-5.15	20.07	0.37	0.09
530	80.75	-3.88	19.12	0.53	0.72	530	80.24	-5.05	20.34	0.63	0.07
677	79.66	-4.39	17.55	2.44	2.66	677	80.24	-4.98	20.11	0.53	0.07
841	78.68	-4.88	16.30	4.10	4.36	841	80.29	-5.02	20.20	0.55	0.02
1014	77.44	-5.36	14.04	6.70	6.47	1014	80.19	-4.78	20.35	0.83	0.16
1203	76.98	-5.77	13.58	7.41	7.24	1203	80.30	-5.03	20.16	0.51	0.03
1388	74.86	-6.45	10.64	11.10	10.68	1388	80.12	-4.74	20.48	0.96	0.29
1556	75.07	-6.60	10.91	10.80	10.35	1556	80.32	-4.89	20.27	0.69	0.07
1738	73.85	-6.96	9.21	12.92	12.27	1738	80.27	-4.71	20.28	0.85	0.02
1906	73.65	-6.96	9.12	13.10	12.58	1906	80.20	-4.82	20.70	1.06	0.14
2148	73.13	-7.30	8.02	14.35	13.38	2148	80.20	-4.76	20.53	0.96	0.14
2335	71.31	-7.60	5.98	17.06	16.10	2335	79.82	-4.28	20.68	1.50	0.82
2624	71.30	-7.77	5.65	17.37	16.11	2624	79.80	-4.64	20.77	1.31	0.85
N/A	N/A	N/A	N/A	N/A	N/A	2847	79.87	-4.47	20.61	1.30	0.73
N/A	N/A	N/A	N/A	N/A	N/A	3015	79.76	-4.35	20.58	1.41	0.92
N/A	N/A	N/A	N/A	N/A	N/A	3203	79.88	-4.55	20.44	1.14	0.71
N/A	N/A	N/A	N/A	N/A	N/A	3461	79.92	-4.65	21.13	1.55	0.64
N/A	N/A	N/A	N/A	N/A	N/A	3773	80.27	-4.50	20.72	1.28	0.02
N/A	N/A	N/A	N/A	N/A	N/A	3983	80.14	-4.44	20.59	1.25	0.25
N/A	N/A	N/A	N/A	N/A	N/A	4176	79.95	-4.37	20.94	1.56	0.59
N/A	N/A	N/A	N/A	N/A	N/A	4361	79.96	-4.23	20.46	1.39	0.57

[0074] As is shown in both Figs. 6 and 7, the medium with the ferrocinium complex (Exp.3B) was substantially more thermally stable than the analogous medium without the additive (Exp. 3A). In fact, while the medium without the additive "failed" or turned blue almost immediately (as indicated by the decreasing b* values and increasing ΔE values), the medium with the ferrocinium complex remained substantially colorless for more than 4,000 hours.

Experiment No. 4

[0075] In this experiment two electrochromic media were prepared by mixing the following materials together in the concentrations provided below.

Experiment No. 4A

Component -	Material	Concentration
Cathodic	Methylviologen BF ₄	16.0mM
Anodic	Di-tert-butyl-diethylferrocene	16.0mM
Additive	None	-
UV-Stabilizer	Tinuvin 384	90.0mM
UV-Stabilizer	Tinuvin P	30.0mM
Thickener	PMMA	3 % by wt.

Experiment No. 4B

Component	Material	Concentration
Cathodic	Methylviologen BF ₄	16.0mM
Anodic	Di-tert-butyl-diethylferrocene	16.0mM
Additive	Di-tert-butyl-diethylferrocinium BF ₄	2.0mM
UV-Stabilizer	Tinuvin 384	90.0mM
UV-Stabilizer	Tinuvin P	30.0mM
Thickener	PMMA	3 % by wt.

5 [0076] As can be seen, Experiment No. 4A does not include an additive and Experiment No. 4B comprises di-tert-butyl-diethylferrocinium BF₄ as an additive. The above-prepared media were associated with electrochromic windows constructed and tested analogous to those used in Experiment No. 3, and L*a*b* data was collected at predetermined intervals, which is provided below.

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Experiment No. 4 – Thermal

Experiment 4A						Experiment 4B					
Hours	L*	a*	b*	ΔE	ΔY	Hours	L*	a*	b*	ΔE	ΔY
0	81.81	-5.43	16.55	0.00	0.00	0	79.76	-6.60	17.34	0.00	0.00
270	77.86	-7.61	10.32	7.69	6.98	270	79.59	-6.13	17.37	0.50	0.30
487	77.43	-8.84	7.99	10.20	7.70	487	81.44	-6.07	18.34	2.03	3.01
753	75.61	-8.77	6.64	12.16	10.69	753	80.18	-5.78	17.35	0.92	0.74
921	74.29	-8.76	5.49	13.78	12.79	921	79.50	-5.55	17.23	1.09	0.46
1185	72.43	-9.49	2.84	17.10	15.65	1185	79.53	-5.53	17.36	1.09	0.41
1448	71.85	-9.73	2.08	18.09	16.51	1448	79.62	-5.48	17.49	1.14	0.25
1595	71.07	-9.92	1.17	19.29	17.66	1595	79.63	-5.43	17.52	1.19	0.23
1759	70.90	-9.95	0.97	19.55	17.91	1759	79.60	-5.46	17.41	1.15	0.28
1932	69.82	-10.45	-0.52	21.46	19.46	1932	79.75	-5.40	17.64	1.24	0.02
2121	70.74	-9.82	0.78	19.76	18.14	2121	79.49	-5.44	17.24	1.20	0.48
2306	69.51	-10.26	-0.77	21.79	19.89	2306	79.51	-5.32	17.60	1.33	0.44
2484	69.38	-10.31	-1.13	22.16	20.08	2484	79.56	-5.40	17.43	1.22	0.35
2666	68.65	-10.58	-2.11	23.41	21.09	2666	79.75	-5.32	17.55	1.30	0.02
2834	68.47	-10.51	-2.24	23.60	21.34	2834	79.55	-5.36	17.47	1.26	0.37
3076	68.34	-10.43	-2.36	23.75	21.52	3076	79.33	-5.30	17.46	1.37	0.76
3263	68.23	-10.61	-2.30	23.80	21.67	3263	79.54	-5.10	17.90	1.62	0.39
3552	67.66	-10.33	-3.00	24.63	22.44	3552	79.22	-5.16	17.52	1.55	0.95
3775	66.81	-10.70	-4.43	26.32	23.57	3775	79.46	-5.09	17.50	1.55	0.53

[0077] Figs. 8 and 9 graphically demonstrate that, once again, the medium without the additive (Exp. 4A) began to fail rapidly relative to the medium comprising the additive (Exp. 4B).

Experiment No. 5

[0078] In this experiment one electrochromic medium was prepared by mixing the following materials together in the concentrations provided below.

Experiment No. 5		
Component	Material	Concentration
Cathodic	Methylviologen BF ₄	34.0mM
Anodic	(6-(tetra-tert-butylferrocenyl)hexyl)triethylammonium BF ₄	2.0mM
Additive	(6-(tetra-tert-butylferrocinium)hexyl)triethylammonium (BF ₄) ₂	21.8mM
UV-Stabilizer	T-butylpentylester of Tinuvin P	50.0mM
UV-Stabilizer	Tinuvin P	30.0mM
Thickener	PMMA	3 % by wt.

[0079] As can be seen, Experiment No. 5 comprises (6-(tetra-tert-butylferrocinium)hexyl)triethylammonium di-tetrafluoroborate as an additive. The above-prepared medium was placed into an electrochromic window comprising two 2x5 inch substrates. The first and second substrates were coated with generally clear, conductive indium/tin oxide (ITO), and were spaced 250 microns apart for accommodating the medium. To simulate prolonged exposure to ultraviolet radiation, the window was placed in a weatherometer at ambient temperature, and was exposed to continuous ultraviolet radiation via an ultraviolet lamp. Subsequently, the temperature inside the weatherometer increased to approximately 70 degrees centigrade due to heat generated by the UV lamp. L*a*b* data was collected at predetermined intervals for the window, which is provided below.

Experiment No. 5 – UV Static

Experiment 5					
Hours	L*	a*	b*	ΔE	ΔY
0	80.21	-5.48	20.13	0.00	0.00
316	80.11	-4.85	20.52	0.75	0.17
434	80.01	-4.97	20.60	0.72	0.35
642	80.07	-4.68	20.67	0.98	0.24
826	80.19	-4.75	20.87	1.04	0.03
994	80.20	-4.77	20.78	0.96	0.01
1182	80.23	-4.72	20.88	1.07	0.04
1350	80.19	-4.71	20.95	1.13	0.03
1534	80.15	-4.62	20.92	1.17	0.10
1702	80.22	-4.57	20.89	1.19	0.02
1870	80.30	-4.56	20.74	1.11	0.16
2107	80.22	-4.53	21.10	1.36	0.02
2289	80.21	-4.48	21.18	1.45	0.00

[0080] As can be seen from the above-collected L*a*b* data, the medium of Experiment 5, with the ferrocinium complex, was substantially more thermally stable than the media without additives in the previous experiments (Exp. 1A, 2A, 3A, 4A). In fact, while such media lacking additives "failed" almost immediately (as is evidenced by the rapidly increasing ΔE values), the color-stabilizing additive of Experiment 5 enabled the electrochromic medium to exhibit only a minimal overall color change after over 2,000 hours of exposure to ultraviolet radiation, as is shown by the small ΔE value. Moreover, the medium of Experiment 5 exhibited only a minimal ΔY value, which further confirms that, indeed, the usage of the above-identified additive provides an effective mechanism to minimize various adverse coloration effects associated with prolonged exposure to ultraviolet radiation.

Experiment No. 6

[0081] In this experiment one electrochromic medium was prepared by mixing the following materials together in the concentrations provided below.

Experiment No. 6

Component	Material	Concentration
Cathodic	Methylviologen BF ₄	34.0mM
Anodic	(6-(tetra-tert-butylferrocenyl)hexyl)triethylammonium BF ₄	21.8mM
Additive	(6-(tetra-tert-butylferrocenyl)hexyl)triethylammonium (BF ₄) ₂	2.0mM
UV-Stabilizer	T-butylpentylester of Tinuvin P	50.0mM
UV-Stabilizer	Tinuvin P	30.0mM
Thickener	PMMA	3 % by wt.

[0082] As can be seen, Experiment No. 6 comprises (6-(tetra-tert-butylferrocenyl)hexyl)-triethylammonium di-tetrafluoroborate as an additive. The above-prepared medium was associated with an electrochromic window constructed analogous to that which was used in Experiment No. 5. In order to simulate prolonged exposure to ultraviolet radiation while cycling between a high transmission state and a low transmission state, as in normal operation of electrochromic windows, the window was placed in a weatherometer at ambient temperature and was exposed to continuous ultraviolet radiation via an ultraviolet lamp while subjected to continuous cycles of electrical potential. Specifically, each cycle consisted of operation of the device at 1.2V for 30 sec. and at 0.0V for 30 sec.; these times allowed the device to undergo darkening to its steady state transmission value and allowed the device to clear completely. L*a*b* data was collected at predetermined intervals for each of the windows, which is provided below.

Experiment No. 6 – UV Cycling

Experiment 6						
Hours	Cycles	L*	a*	b*	ΔE	ΔY
0	0	79.07	-5.44	19.94	0.00	0.00
263	15809	79.91	-5.23	20.60	1.09	1.47
489	29323	78.77	-5.13	20.12	0.47	0.52
648	38868	79.00	-5.13	20.37	0.53	0.12
764	45856	78.84	-5.04	20.25	0.56	0.40
926	55573	79.02	-5.07	20.39	0.58	0.09
1091	65452	79.74	-5.02	21.02	1.34	1.17

1211	72679	79.19	-4.98	20.62	0.83	0.21
1354	81239	79.82	-5.09	20.77	1.17	1.31
1562	93729	78.15	-4.96	20.74	1.31	1.58
1709	102561	78.83	-4.80	20.52	0.90	0.42
1936	116173	78.75	-4.86	20.73	1.03	0.55
2105	126285	79.03	-4.84	20.91	1.14	0.07
2292	137545	79.47	-4.89	21.07	1.32	0.70
2509	150513	79.48	-4.82	21.10	1.38	0.72
2751	165086	79.11	-4.78	21.39	1.59	0.07
2926	175571	78.42	-4.86	20.94	1.33	1.12
3069	184136	78.26	-4.77	21.09	1.56	1.40
3215	192907	78.55	-4.84	21.29	1.57	0.90
3406	204343	78.19	-4.73	21.18	1.68	1.51
3819	229113	77.20	-4.38	20.68	2.27	3.19
3983	238974	77.51	-4.41	20.97	2.13	2.67
4146	248751	77.96	-4.35	21.26	2.04	1.91
4389	263316	77.58	-4.29	21.19	2.26	2.55
4628	277687	78.47	-4.43	21.45	1.91	1.04
4797	287804	77.53	-4.36	21.43	2.40	2.63
4963	297777	77.36	-4.31	21.21	2.41	2.92
5144	308625	77.18	-4.21	21.00	2.49	3.22
5360	321593	78.78	-4.55	21.77	2.06	0.50
5598	335854	77.96	-4.41	21.31	2.04	1.91
5821	349241	77.98	-4.33	21.40	2.13	1.87
5987	359220	78.16	-4.38	21.59	2.16	1.57
6190	371383	77.77	-4.32	21.34	2.21	2.23
6361	381636	77.71	-4.34	21.43	2.30	2.33
6545	392705	78.48	-4.21	21.75	2.27	1.02
6785	407108	77.59	-4.27	21.55	2.48	2.53
7010	420595	77.06	-4.29	21.69	2.90	3.42
7211	432632	77.80	-4.43	21.95	2.58	2.18
7401	444033	77.66	-4.39	21.60	2.42	2.41
7586	455140	77.65	-4.47	21.68	2.45	2.43
7677	460620	78.05	-4.65	21.79	2.26	1.75
7819	479150	77.94	-4.53	22.16	2.65	1.94
7946	486744	76.85	-4.46	21.70	3.00	3.77
8088	495356	77.82	-4.65	22.34	2.82	2.14
8231	503899	76.74	-2.10	22.74	4.94	3.95
8374	512756	77.18	-4.27	23.82	4.47	3.22
8517	521621	77.13	-4.60	23.76	4.37	3.30
8805	541110	78.14	-4.76	23.51	3.75	1.60
9117	559983	76.68	-4.62	23.94	4.73	4.05
9260	568826	75.84	-4.70	22.47	4.17	5.42
9426	579146	77.06	-4.63	23.52	4.18	3.42
9585	589245	76.26	-5.49	23.54	4.57	4.74
9742	598978	76.37	-5.23	23.77	4.69	4.56
10011	616835	75.93	-5.40	24.54	5.57	5.28

[0083] The medium of Experiment 6, with the ferrocinium complex, was substantially more thermally stable than the media without additives in the previous experiments (Exp. 1A, 2A, 3A, 4A). In fact, while such media lacking additives "failed" almost immediately (as is evidenced by the rapidly increasing ΔE values), the color-stabilizing additive of Experiment 6 enabled the electrochromic medium to exhibit only a minimal overall color change after over 10,000 hours of exposure to ultraviolet radiation while undergoing multiple cycles of application and removal of an electrical potential difference, as is shown by the small ΔE value. Moreover, the medium of Experiment 6 exhibited only a minimal ΔY value, which further confirms that, indeed, the usage of the above-identified additive provides an effective mechanism to minimize various adverse coloration effects associated with prolonged exposure to ultraviolet radiation and electrical potential cycling.

Experiment No. 7

[0084] In this experiment one electrochromic medium was prepared by mixing the following materials together in the concentrations provided below.

Experiment No. 7

Component	Material	Concentration
Cathodic	Methylviologen BF_4	34.0mM
Anodic	(6-(tetra-tert-butylferrocenyl)hexyl)triethylammonium BF_4	21.8mM
Additive	(6-(tetra-tert-butylferrocinium)hexyl)triethylammonium $(\text{BF}_4)_2$	2.0mM
UV-Stabilizer	T-butylpentylester of Tinuvin P	50.0mM
UV-Stabilizer	Tinuvin P	30.0mM
Thickener	PMMA	3 % by wt.

[0085] As can be seen, Experiment No. 7 comprises (6-(tetra-tert-butylferrocinium)hexyl)-triethylammonium di-tetrafluoroborate as an additive. The above-prepared medium was associated with an electrochromic window constructed analogous to that which was used in Experiment No. 5. In order to simulate exposure to prolonged elevated temperatures while cycling between a high transmission state and a low transmission state, as in normal operation of electrochromic windows, the window was placed in an oven

at 70 degrees centigrade and was subjected to continuous cycles analogous to the cycles used in Experiment 6. L*a*b* data was collected at predetermined intervals for the window, which is provided below.

Experiment No. 7 – 70°C Cycling

Experiment 7						
Hours	Cycles	L*	a*	b*	ΔE	ΔY
0	0	79.82	-5.39	19.65	0.00	0.00
292	17542	79.51	-4.90	20.16	0.77	0.54
556	33351	79.50	-5.01	19.86	0.54	0.56
703	42166	79.57	-4.91	19.97	0.63	0.44
868	52054	79.75	-5.33	19.79	0.17	0.12
1041	62466	79.42	-5.50	20.12	0.63	0.70
1227	73619	79.75	-5.30	20.15	0.51	0.12
1416	84981	79.74	-5.34	20.07	0.43	0.14
1584	95028	79.38	-5.04	19.93	0.63	0.77
1755	105307	79.77	-5.39	19.97	0.32	0.09
1926	115549	79.59	-5.16	19.88	0.40	0.40
2168	130068	79.47	-5.09	19.80	0.48	0.61
2362	141736	79.33	-4.96	19.84	0.68	0.86
2625	157527	79.57	-4.96	20.02	0.62	0.44
2849	170916	79.48	-5.24	20.00	0.51	0.59
3012	180705	79.36	-4.97	20.41	0.98	0.80
3185	191100	79.11	-5.10	19.93	0.82	1.24
3443	206587	79.48	-4.74	20.42	1.06	0.59
3755	225311	79.59	-5.12	20.21	0.66	0.40
3958	237478	79.52	-5.12	19.93	0.49	0.52
4151	249060	79.41	-4.94	20.24	0.85	0.72
4336	260177	79.38	-4.83	20.24	0.92	0.77
4506	270365	79.31	-4.91	20.27	0.94	0.89
4747	284799	79.22	-4.98	20.21	0.92	1.05
5109	306568	78.57	-4.71	20.25	1.54	2.17
5279	316755	78.99	-4.57	20.27	1.32	1.45
5457	327435	78.73	-4.99	20.12	1.25	1.90
5723	343375	79.47	-4.82	20.46	1.05	0.61
5898	353861	79.04	-4.84	20.24	1.12	1.36
6157	369409	79.24	-4.70	20.42	1.19	1.01
6348	380851	78.88	-4.73	20.39	1.37	1.64

5

[0086] As is shown in the above table, the medium with the ferrocinium complex (Exp.7) was substantially more thermally stable than the media without additives in the previous experiments (Exp. 1A, 2A, 3A, 4A). In fact, while such media lacking additives "failed" almost immediately (as is evidenced by the rapidly increasing ΔE values), the color-

stabilizing additive of Experiment 7 enabled the electrochromic medium to exhibit only a minimal overall color change after over 6,000 hours of exposure to elevated temperatures while undergoing over 375,000 cycles of application and removal of an electrical potential difference, as is shown by the small ΔE value. Moreover, the medium of Experiment 7

5 exhibited only a minimal ΔY value, which further confirms that, indeed, usage of the above-identified additive provides an effective mechanism to minimize various adverse coloration effects associated with prolonged exposure to elevated temperatures and electrical potential cycling.

[0087] As can be seen from the above-provided experiments, the incorporation of one
10 or more of the disclosed additives substantially improves the color-stability of an electrochromic medium – even under oxidative environments, elevated temperatures, prolonged ultraviolet radiation, or cyclical applications of an electrical potential difference.

[0088] While the invention has been described in detail herein in accordance with certain preferred embodiments thereof, many modifications and changes therein may be
15 effected by those skilled in the art. Accordingly, it is our intent to be limited only by the scope of the appending claims and not by way of details and instrumentalities describing the embodiments shown herein.